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A Comparison of the Time of Set of Similarly Constituted Gels at Various Temperatures

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A COMPARISON OF THE TIME OF SET OF SIMILARLY CONSTITUTED GELS AT VARIOUS TEMPERATURES

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INTRODUCTION

This investigation was undertaken with the purpose of obtaining more data on the question of the existence of thermally reversible silicic acid gels, i.e., silicic acid gels which would reliquify on heating.

Some work was done in the highly basic region at 21° and 40° C. An attempt was made to use the Leeds and Northrup glass electrode apparatus present in the Union College Chemical Laboratory which, however, failed, although Spittle,[1] using this apparatus, apparently met with some success.

In order to obtain complete data on the change of time of set with temperature of gels having the same composition as well as providing a convenient reference for such gels, two curves, one at 25° C and one at 40° C, were obtained showing the time of set as a function of increasing amounts of acid. The necessary P.h. curves are included.

HISTORICAL

Silicic acid gels have been known for many years. An early record of such gels shows that they were prepared by Berzelius (2) about 1820, although certain references indicate that previous work had been done on such gels. The temperature effects mentioned below were thoroughly investigated by Holmes (3) and others.

Two important questions arose from this early work: the first concerning the mechanism by which the gel set, the second relating to the gel structure.

Three theories were propounded in explanation of the second question. These were (a) The Emulsion Theory, (b) The Cellular Theory, and (c) The Fibrillar or Micellar Theory. The most conclusive experimental evidence is in favor of the last theory. According to this theory the silicic acid molecules react by splitting off water to form a "brush heap" structure. (See Hurd, C. B., Chem. Rev., Vol. 22, #3, 485 (1938).) This theory, in addition to receiving experimental support, also offers an explanation of the first question, the setting mechanism.

Since this investigation was mainly concerned with the process by which the gel sets, this reaction and the known facts relating to it will be summarized.

The reaction shown below was the proposed reaction:

$$x\,H_2SiO_3 = H_2\,Si_x\,O_{(2x+1)} + (x-1)\,H_2O$$

or: $$x\,H_4SiO_4 = H_{(2x+2)}\,Si_x\,O_{(3x+1)} + (x-1)\,H_2O$$

If this reaction takes place one should be able to determine certain facts relating to it. Hurd (4) found that a linear relationship existed between the log time of set and the reciprocal of the absolute temperature. From

this a quantity similar to the energy of activation was computed. Consistent values for this activation energy were obtained from the data.

Another important question concerning this reaction was that of the extent of its reversibility due to temperature changes. It appeared at first that a rise in temperature favored the formation of the products at the right as the time of set was decreased upon raising the temperature. Fosotti,(5) however, working in the basic region, found that above a certain P.h. (about 10.45) a rise in temperature caused an increase in the time of set. While this is by no means a conclusive proof of the existence of a reversible gel, yet it is indicative of the most likely region in which a reversible gel would be found.

Spittle, (1) using the Leeds and Northrup glass electrode to be described, also did some work in the basic region. His results are described in his thesis.

EXPERIMENTAL

Preparation of solutions

A seven liter solution of E-brand sodium silicate in CO_2 - free distilled water was prepared. This solution was titrated against a secondary standard of sulfuric acid using methyl orange as indicator. The normality of the silicate so ution was 1.669N. The sulfuric acid was titrated against standardized NaOH. The indicator used was phenol phthalime. The sodium hydroxide was titrated against a primary standard of oxalic acid containing two molecules of water of hydration using phenol phthalime as indicator.

A seven liter solution of glacial acetic acid in CO_2 - free distilled water was also prepared. This solution was titrated against the standardized sodium hydroxide solution. Its normality was found to be 1.449. Phenol phthalime was used as indicator.

Constant temperature baths

Three constant temperature baths were used. A bath at 40° C, one at 25° C, and one at 21° C.

The bath at 40° C was arranged in the usual manner, being provided with a motor stirrer, knife heater, and bimetallic thermal regulator. The room was kept at as high a temperature as possible in order to keep the bath from cooling too rapidly.

The 25° C bath was provided with a motor stirrer, knife heater, and a mercury-toluene thyraton regulator. This regulator has been described in the literature.

The 21° C bath was provided with a motor stirrer; the large volume of water and the proximity of the bath temperature to that of the room served to hold the temperature constant. In addition, water of desired temperature

was added at frequent intervals to aid in holding the temperature constant at 21° C.

P.h. measurements

In the acedic region P.h. measurements were made using the quinhydrone electrode. This apparatus is amply described in the literature.

P.h. measurements in the basic region were made with the Beckman P.h. meter. The circuit used in this meter as well as other pertinent facts concerning it are discussed in The Glass Electrode, by Dole.

The writer's attempt to use the Leeds and Northrup glass electrode proved unsuccessful, yet his experience with it as well as some of the theory in relation to it will be described because of its importance in measuring the P.h. of basic gels due to its great convenience and accuracy in handling.

A piece of glass tubing of 015 Corning glass about 6 mm. in diameter is selected and a bulb blown in one end in the usual manner, care being taken to use as low a temperature as is possible to work the glass. The bulb was carefully cleaned, dried, and about one third of it filled with app. .1NHCl.

The inner electrode used usually consists of a quinhydrone electrode, although somewhat better results can be obtained using several others, in particular a silver-silver chloride electrode. In preparing the quinhydrone electrode a platinum wire was sealed in the end of a piece of glass tubing, a pinch of quinhydrone added to the .1NHCl solution, and the electrode inserted in the bulb in a manner analogous to that used with the inner reference electrode of the calomel cell. The glass electrode is well shaken in order

to completely saturate the .1M KCl solution with the quinhydrone. A side-arm calomel cell is prepared for use as a reference electrode. Such a cell will give values for the e.m.f. developed which are in agreement with those given by a quinhydrone electrode, i.e., the standard electrode potential of both cells will be the same.

The circuit for the operation of the glass electrode using the Leeds and Northrup #7652 Potentiometer and the Leeds and Northrup #2480-C dual galvanometer is shown below.

In using the glass electrode, it, together with the reference electrode (usually a calomel cell), is immersed in the solution, the P.h. of which is to be measured, and allowed to come to temperature. The e.m.f. developed by the cell is then measured and converted to P.h. readings.

Only a general qualitative discussion of the theory will be undertaken. For a more concise, quantitative presentation of the theory discussed from the view point of thermo-dynamics, see Bole (above reference).

According to present views, the glass is permeable to hydrogen ions. Thus the outer and inner surfaces of the glass develop potentials and these potentials vary as the potential of a hydrogen electrode. Such electrodes

are said to have the hydrogen electrode function, i.e., a linear relationship exists between the e.m.f. developed and the P.h. of the solution. While the potential of inner surface of the glass varies as the hydrogen electrode, so also does the inner reference platinum electrode. Thus the potential between this electrode and the inner surface of the glass remains constant, and hence the measured variation of e.m.f. with P.h. occurs between the reference calomel cell and the outer glass surface. As long as the glass surface possesses only the hydrogen electrode function, the analytical linear relationship between the cell e.m.f. and solution P.h. may be used to compute the P.h., i.e., the expression $P.h. = mE + b$. However, in solutions possessing sodium ions most glasses including the 015 Corning glass also possess a sodium ion electrode function. Here the above mentioned linear relationship no longer holds and the measured P.h. is observed to be less than the actual P.h. Correction curves have been devised, and reference may be made to them in correcting for this discrepancy.

It was correctly observed that if a glass could be made which was permeable to hydrogen ions only, the glass would function as a hydrogen electrode in the presence of disturbing ions. As a result, glasses have been made which show little or no deviation even in solutions of high sodium ion concentration.

A correction must also be made for the asymmetrical potential, which is the potential existing between the inner and outer surfaces of the glass when the solutions on both sides are of the same P.h. The conventions regarding the sign of this potential may be found in the previously mentioned book by Dole.

The arbitrariness concerning the .1NHCl solution was noted and an attempt made to determine the effect of dilution of this solution upon the cell e.m.f. It was found that a large deviation in the strength of the .1NHCl used produced only a small change in the observed e.m.f. Hence the HCl solution need

only be app. .1E in order to obtain an E° value comparable to that of the quinhydrone electrode. However, it must be remembered that the equipment used was faulty and therefore the results obtained are not to be relied on too closely.

Gel Mixtures

The total volume of the gel mixture and the volume of the sodium silicate solution were maintained constant at 200 c.c. and 48.6 c.c., respectively.

The volume of acid was varied to give solution with the desired P.h.

Procedure

The proper amounts of silicate, acid, and water solutions were pipetted into clean dry electrolytic beakers, the acid and water mixture being placed in one beaker while the silicate solution was put in the other.

These solutions were then placed in the desired constant temperature bath and allowed to come to bath temperature.

The two solutions were then well mixed and part of the resulting solution poured into a 100 ml. K beaker which was quickly replaced in the bath. The time of mixing was carefully noted. If a P.h. measurement was to be made, a portion of the solution in the electrolytic beaker was poured into a second K beaker, the desired electrodes inserted into this solution and allowed to come to temperature, after which a potentiometric reading was taken. These e.m.f. readings were taken in a separate beaker because, when using the quinhydrone electrode, the quinhydrone added to the solution might affect the time of set of the gel.

The time of set was determined using the tilted rod method.

P.h. measurements involving the Beckman P.h. meter were made using a buffer solution of P.h. 9.84. After a measurement had been made on a gel solution of unknown P.h., the meter was restandardized using the same buffer.

Deviations from the P.h. value of this buffer were added or subtracted to the recorded P.h. for the gel solutions. Before P.h. measurements were taken, a portion of the solution to be tested was used to rinse the electrodes. After setting, the highly basic gels were placed in a steam bath for one hour and then tested for reversibility.

RESULTS

1. No reversible gels were found.

2. A plot of two curves, one at 40° and one at 21° C, showing variation of time of set against increasing amounts of acid for highly basic gels was obtained which possessed the following properties:

   (a) The time of set for gels having the same composition was higher at 21° than at 40° C in the highly basic region.

   (b) The curves crossed at a lower P.h., reversing the above behavior. It was not possible to determine the P.h. of the gels setting at 21° when the crossing occurred.

   (c) The curves recrossed at a still lower P.h. and it was again observed that the gel setting at 21° had a longer time of set than those of the same composition setting at 40° C.

It is impossible to draw a definite conclusion concerning this behavior. It must be remembered that the P.h. of an alkaline solution is reduced when the temperature is raised. Because P.h. measurement could not be made at 40° C, it was impossible to compare basic gels of the same composition on the basis of their P.h. The possible reasons for these results will now be discussed.

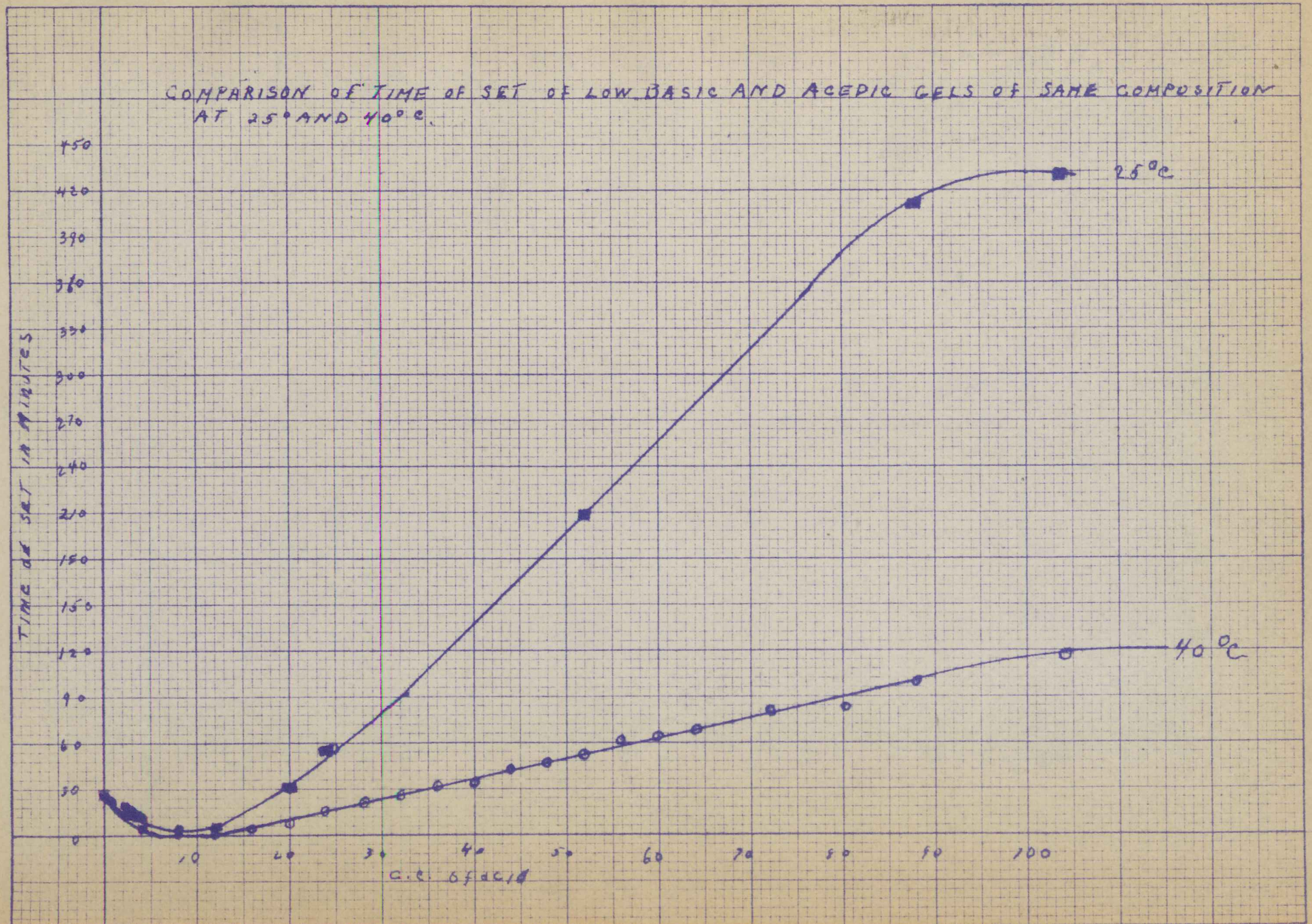
Other factors being constant, the time of set depends upon the temperature at which the gel sets and upon its P.h. That it depends on both is obvious from the following: In the acedic region gels of the same composition possess the same P.h. at any temperature. Since the time of set in this region is different at different temperatures for such gels, we conclude that the temperature is a factor affecting the time of set. Again the time of set of a gel varies when the amount of acid is varied at constant temperature. Hence we infer that the P.h.

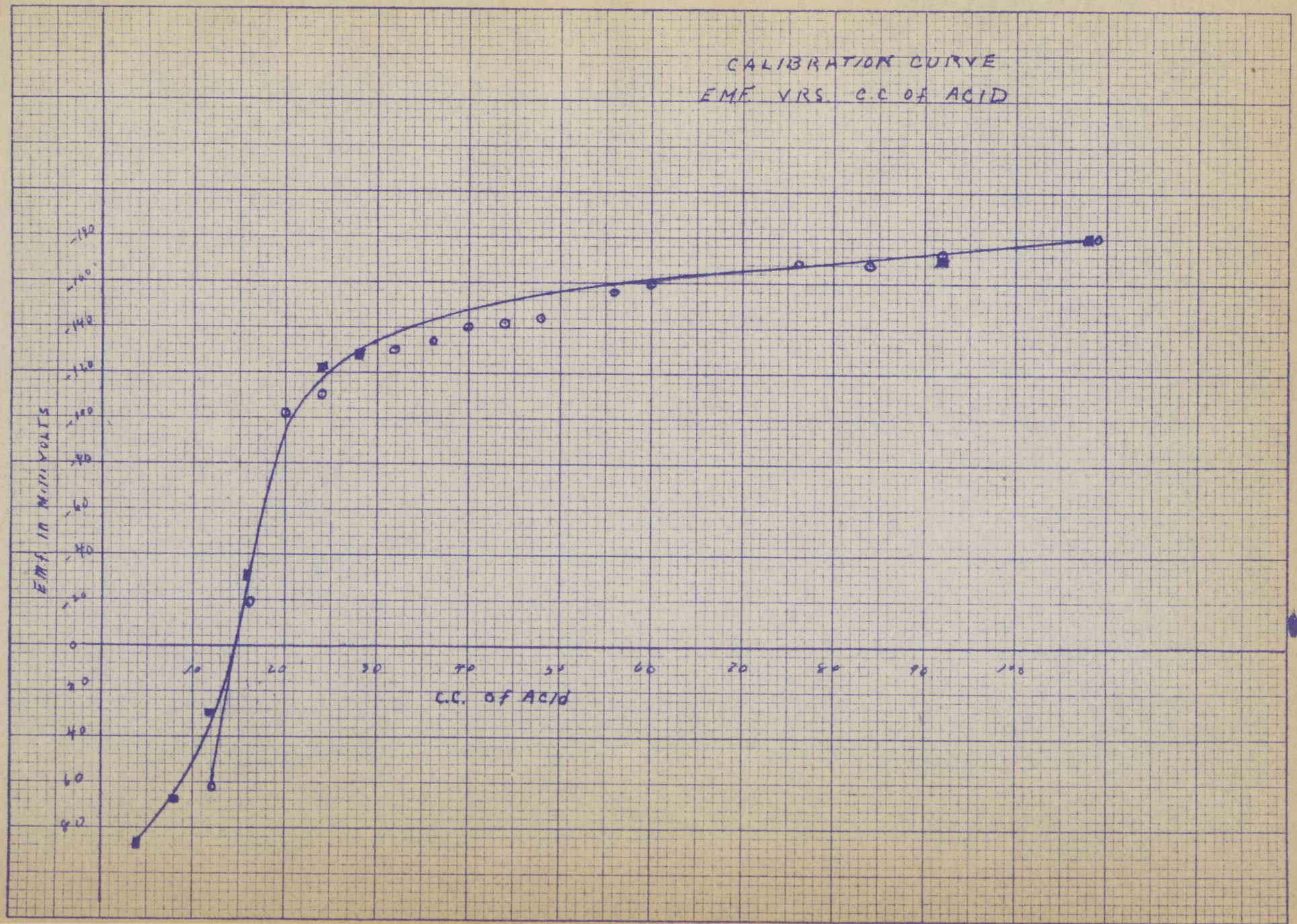
is also a factor affecting the time of set. While in the acedic region, therefore, the temperature alone affects the time of set of gels having the same composition, in the basic region both the temperature and the P.h. affect the time of set of such gels.

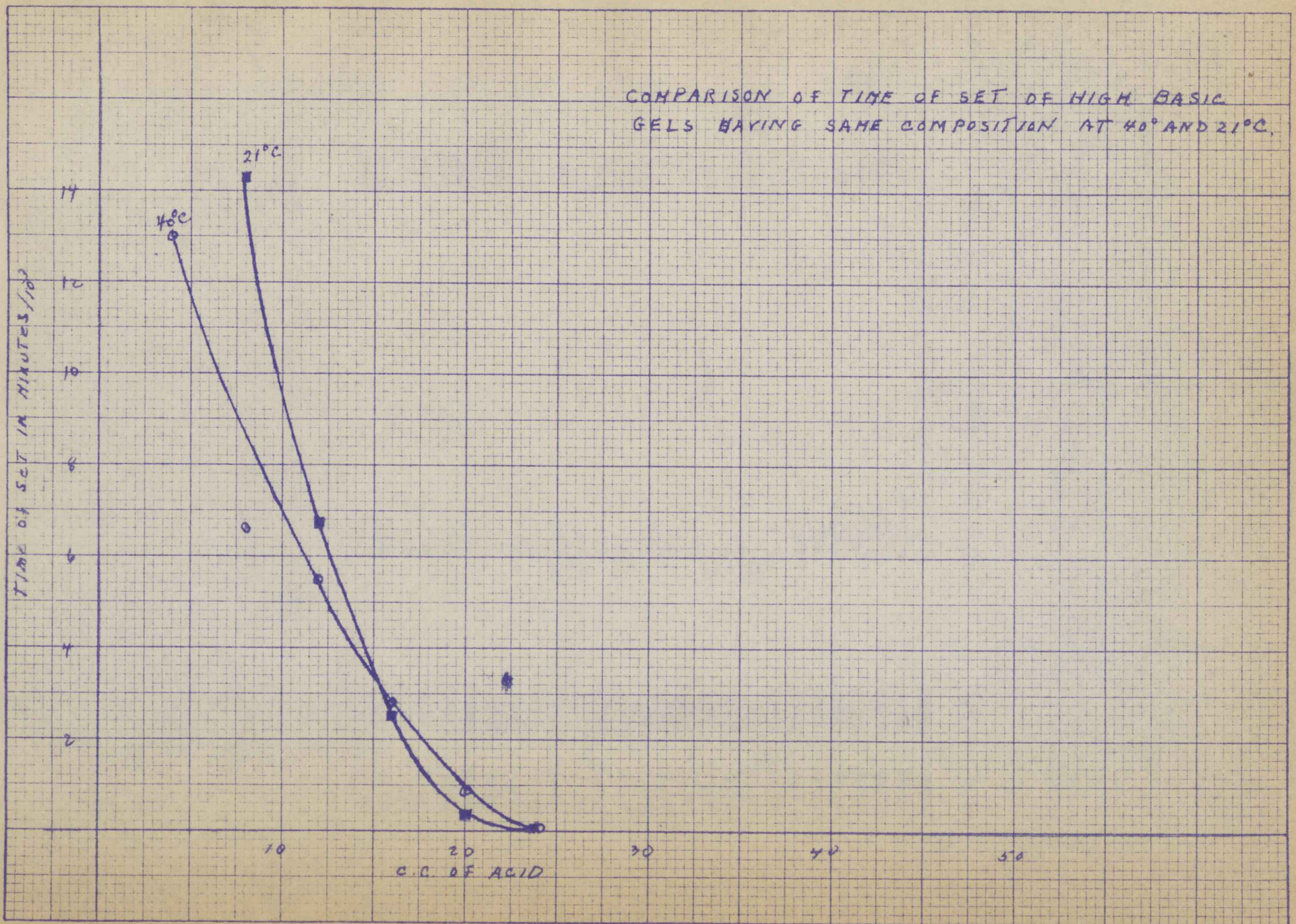
Let us consider the combined effect of the temperature and P.h. on the time of set of similarly constituted gels in the basic region, starting with gels of P.h. 10.45, as the P.h. of the gels increases. In the lower basic region the change of P.h. with change in temperature is slight, resulting in a predominance of the temperature effect, and we observe the results already noted by Pometti (5), i.e., that a rise in temperature results in a longer time of set. As the P.h. increases, however, greater deviations of P.h. with temperature occur, the effect of P.h. on the time of set increases, and, although the temperature effect alone might show that a rise in temperature lengthens the time of set, the resultant effect of both temperature and P.h. might actually cause a reduction in the time of set (for the P.h. would be lower at the higher temperature). Hence the curves would recross as shown.

It is possible that although the P.h. effect does increase, the resultant effect may still be largely due to the temperature factor. This would mean that, if the P.h. was held constant in gels of the same composition at different temperatures, the recrossing of the curves in the higher basic region would still be observed and Pomotti's statement that a rise in temperature lengthens the time of set for gels of P.h. greater than about 10.45 would be true only for a relatively small part of the basic region.

5. Two curves were obtained, one at 40° and one at 25° C, covering most of the acedic region. These curves are shown in order that a complete picture of the change in time of set of gels at two different temperatures might be had over the whole P.h. range as explained in the Introduction.


COMPARISON OF TIME OF SET OF LOW BASIC AND ACEPIC GELS OF SAME COMPOSITION AT 25° AND 40° C.
TIME OF SET IN MINUTES
450
420
390
360
330
300
270
240
210
180
150
120
90
60
30
0
10
20
30
40
50
60
70
80
90
100
C.C. OF ACID
25°C
40°C


CALIBRATION CURVE
EMF VRS. C.C. OF ACID
EMF IN MILLIVOLTS
C.C. OF ACID
10
20
30
40
35
60
70
80
90
100


COMPARISON OF TIME OF SET OF HIGH BASIC
GELS HAVING SAME COMPOSITION AT 40° AND 21°C.
21°C.
40°C
TIME OF SET IN MINUTES/10
14
12
10
8
6
4
2
10
20
30
40
50
C.C. OF ACID

VARIATION OF TIME OF SET WITH VARYING AMOUNTS OF ACID AT 40° C

All gel mixtures had a constant volume of 200 c.c. and contained 46.6 c.c. of sodium silicate solution. The concentration of Na^+ ions was .390 g. mol./lit.

c.c. of acid	conc. of HAC	time of set (min.)	m.v.	P.h.
17.1	.123 g. mol./lit.	about 18,480	none	none
21.1	.152	12,882	none	none
25.1	.181	6,636	none	none
29.1	.208	5,358	none	none
33.1	.239	2,700	none	none
37.1	.268	855	none	none
41.1	.297	27	none	none
45.1	.326	3	none	none
49.1	.355	.5	/68	8.51
53.1	.384	1	-18	7.00
57.1	.413	4.5	-102	5.65
61.1	.442	7	-110	5.52
65.1	.471	16	-128	5.25
69.1	.500	21	-150	5.20
73.1	.529	26.5	-153	5.14
77.1	.558	32	-140	5.04
81.1	.588	34.5	-142	5.00
85.1	.617	43.5	-144	4.97
89.1	.646	47	none	none
93.1	.675	52	-156	4.76
97.1	.704	61	-160	4.72
101.1	.733	64	none	none
105.1	.762	68	none	none
113.1	.791	80	none	none
121.1	.820	82	-168	4.59
129.1	.849	100	-172	4.52
145.1	.878	118	-180	4.40

Normality of sodium silicate solution: 1.669N

Normality of acetic acid solution: 1.449N

VARIATION OF TIME OF SET WITH VARYING AMOUNTS OF ACID AT 21° C

All gel mixtures had a constant volume of 200 c.c. and contained 46.6 c.c. of sodium silicate solution. The concentration of Na^+ ions was .390 g. mol./lit.

c.c. of acid	conc. of HAC	time of set (min.)
17.1	.123 g. mol./lit.	undetermined
21.1	.152	about 21,600
25.1	.181	14,220
29.1	.208	6,690
33.1	.239	2,460
37.1	.268	521
41.1	.297	25

VARIATION OF TIME OF SET WITH VARYING AMOUNTS OF ACID AT 25° C

All gel mixtures had a constant volume of 200 c.c. and contained 46.6 c.c. of sodium silicate solution. The concentration of Na^+ ions was .390 g. mol./lit.

c.c. of acid	conc. of HAC	time of set (min.)	m.v.	P.h.
41.1	.297 g. mol./lit.	24.5	+89	9.10
45.1	.326	4	+69	8.84
49.1	.355	2	+30	8.17
53.1	.384	2	-31	7.14
81.1	.442	31	-122	5.58
65.1	.471	54	-124	5.55
93.1	.675	209	none	none
129.1	.849	410	-170	4.78
145.1	.878	430	-180	4.62

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